ALKALINE IONEX MEMBRANES

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Introduction

The possible application of anion exchanging membranes in chemical power sources is an interesting challenge. For example, its alkaline reaction means much lower requirements on the corrosion resistance of all materials used in power sources. We have measured the impedance and resistivity towards carbonate ions of several samples of membranes. AFC offer several advantages over the more commonly used and researched PEMFC. The kinetics of the electrode reactions are superior in an alkaline environment (AFC) compared to acidic environment (PEMFC). The inherently faster kinetics of the reactions in an alkaline fuel cell allows the use of non-noble metal electro-catalysts like nickel, silver, and platinum. AFC exhibit much higher current densities and electrochemical efficiencies at comparable temperatures over PEMFC. Moreover, AFC electrodes are stable and not prone to poisoning caused by carbon monoxide (CO), which poisons the platinum catalyst of the PEMFC. Therefore, considering the cost and simplicity of operation, AFC are more advantageous as compared to PEMFC and have better prospects in the commercialization of the fuel cells. However, AFC are inherently plagued by problem of carbon dioxide poisoning, which limits their use as air-breathing energy sources. The poisoning reaction depletes the alkaline KOH electrolyte directly by the following reaction:

$$CO_2+2KOH(aq)\rightarrow K_2CO_3(aq)+H_2O \qquad (1)$$

The problem of membrane fuel cells was discussed by Fauvarque *et al.* [1] who suggested an entirely new anion exchanging membrane for hydrogen / oxygen fuel cell. Their lower corrosion activity offers the possible application of electro catalysts not containing any platinum metal. Some modifications of their membranes are described in this paper.

Experimental

Following membranes were used for comparison:

- Anion exchanging heterogeneous membrane RALEX AM

  (MEGA Inc., Czech Republic)
- Anion exchanging membrane manufactured according to J.F. Fauvarque et al [2]. This material was synthesized by addition of DABCO (diazobicyclooctane) on polyepichlorhydrine and trimethylamine. APE screen was soaked by the liquid form of the ion exchanger and dried; this procedure was repeated several times.

The procedure was described by Fauvarque [*L.C.*] but a condensation of polyepichlorhydrine with diazo bicycle octane (DABCO) followed by the addition of a ternary aliphatic amine. This way, a colloid was obtained and carefully deposited onto a PE screen or similar material. Then, it was hardened using thermal irradiation.
The membrane was compared to the membrane RALEX AM (Mega Inc., Straz pod Ralskem, Czech Republic).

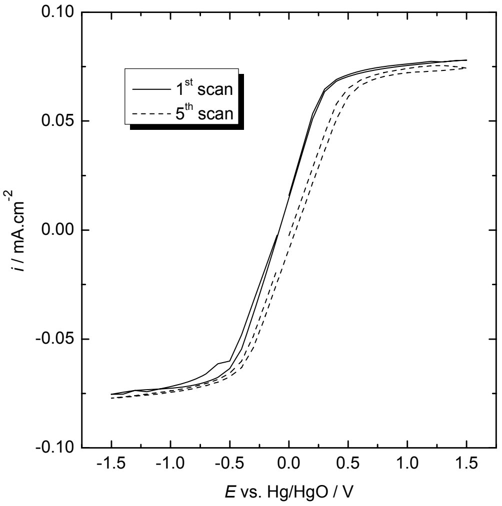
Results and discussion

Cycling voltammetry at the scan rate of 10mV.s^{-1} and impedance spectroscopy were the main methods performed on the potentiostat Autolab instrument (Ecochemie, The Netherlands) (see Fig.1, 2).
The instrument was connected to a 4-probe electrode measurement cell with current platinum electrodes and reference Hg-HgO, RCE101 electrodes. Membrane resistance was determined by extrapolating the linear part of the Nyquist plot to the real axis of the impedance spectrum. To measurement the membrane conductivity at the relative humidity 100%, the sample was stored in distilled water for 48 hours and 48 hours in 1M KOH. Experiments were performed in 1M solution of potassium hydroxide (KOH). This measurement gave the ionic conductivity of the membrane in an electrolyte. Impedance measurements using the FRA-2 module with the frequency range from 10 kHz to 0,1Hz. The equivalent circuit for measure cell can be expressed as a resistance Rs in the series with the constant phase element CPE1 parallel Rp (boundary between membrane and electrolyte) (see Fig. 5).
The membrane resistance was determined from the impedance spectrum. Ionic conductivity σ (S.cm^{-1}) of membrane was determined owing to the following relation:

$$\sigma = \frac{l}{R_{MEM}.S} \qquad (2)$$

where l is the membrane thickness (cm), S is the membrane surface exposed to the electric field (cm^2), R_{MEM} the membrane resistance (Ω).
We have tested the electrochemical stability of the membrane by chronopotentiometrical method. Both parts were filled by 1M KOH at the beginning and constant current (50 mA/cm^2 approx.) was applied. After a steady state had been reached, the electrolyte was replaced by the 1 M solution of K_2CO_3 and the steady state was reached again. Finally, the vessel was filled by the 1M KOH again. The exchange of electrolytes was performed without interruption of electric circuit. The change of voltage was recorded. Impedance spectroscopy of the membrane measured in the steady state and in an open circuit conditions. The course of voltage is indicated in Figs. 3 and 4, from which we see the increase of resistance in the system by the introduction of carbonates, as well as the comparison between membranes RALEX AM and DABCO.
We have tested ionomer DABCO for FC electrodes as a binding material. The ionomer substitute a PTFE in an electrode matrix. We have followed the Oxygen Reduction Reaction (ORR) in an alkaline fuel cell cathode. Glassy carbon disc ring (RDE) was used to evaluation ORR. The active layer was deposited from an ink containing carbon black,

isopropanol, distilled water and 20 wt% of ionomer. The ink was homogenized by sonical. The measurement was performed in 1M KOH in a three probe system (see Fig.6).



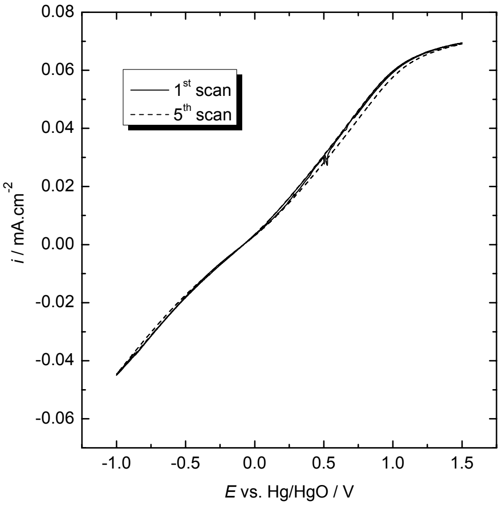
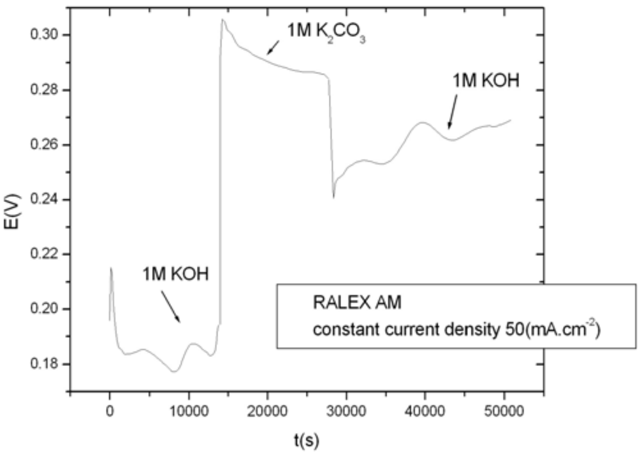


Fig. 1 *(left) cyclic voltammogram of the RALEX AM*
Fig. 2 *(right) cyclic voltammogram of DABCO*



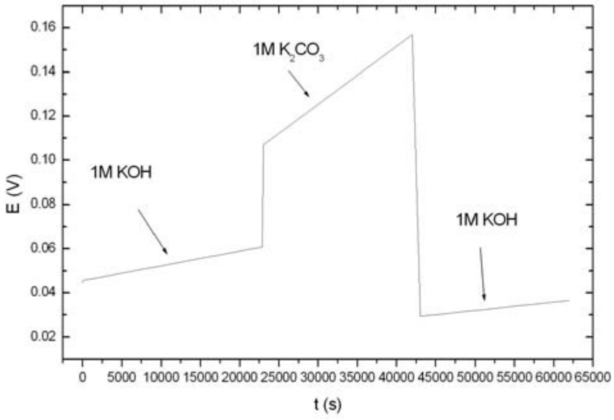
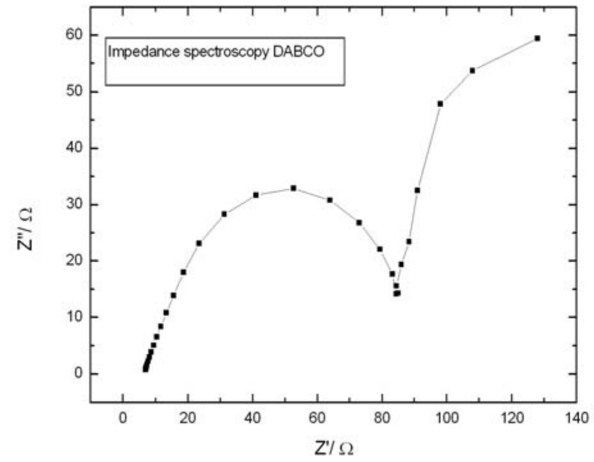


Fig. 3 *(left) chronopotentiometrical method of RALEX AM*
Fig. 4 *(right) chronopotentiometrical method of the DABCO*



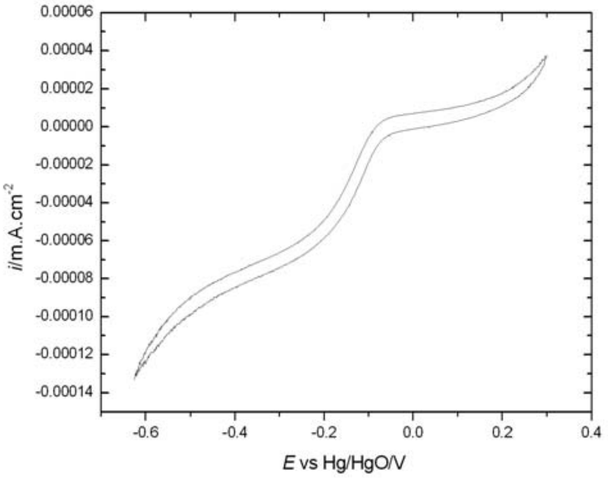


Fig. 5 *Impedance spectrum of DABCO membrane*
Fig. 6 *Cyclic voltammogram of RDE*

Conclusions

The ionic conductivity of DABCO membrane is σ=30mS.cm^{-1}. (2) Our aim is checking the possibility of a DABCO membrane with a catalyst MnO_x/C [3] for positive electrode and Ni/C (or Raney Ni in a passive form) for negative electrode in H_2-O_2 FC.

Acknowledgements

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